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STUDY OF PREIGNITION PROCESSES IN ZIRCONIUM, TITANIUM, AND ZIRCONIUM HYDRIDE

B. M. Zlobinskii, et al

Foreign Technology Division
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B. M. Zlobinskiy, V. M. Maltsev and V. V. Kurylev

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By: B. M. Zlobinskiy, V. M. Maltsev and V. V. Kurylev

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А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ë in Russian, transliterate as yë or ë. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

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GRAPHICS DISCLAIMER

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RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}
rot	curl
lg	log

STUDY OF PREIGNITION PROCESSES IN ZIRCONIUM, TITANIUM, AND ZIRCONIUM HYDRIDE

B. M. Zlobinskiy, V. M. Maltsev
and V. V. Kurylev

Moscow Institute of Steel and Alloys,
The Department of Industrial Safety
Measures

The study of preignition processes stemmed from the need to more fully explain the ignition and combustion mechanisms of metals. The experiments were carried out on particles of electrolytic zirconium (99.96% Zr), megnetothermic titanium (94.6% Ti), and zirconium hydride (ZrH_2).[1]

Microphotographing technique is being used to estimate the growth of oxide films on metal particles (ranging from 100 to 520 μm) under conditions of dynamic heating. Graphite plate (MG-1) with the dimensions of 8×18×5 mm was used as the heater-substrate. The heating was accomplished by an electrical current from a network of alternating voltage, which was fed to the plate through a universal power unit. The heating rate was regulated in the range from 20 to 90 deg/s. Temperature of the particles

[1]For 1 g of metal there is 240 cm^3 of hydrogen and less than 0.2 cm^3 of oxygen.

and the heating rate was recorded by means of Chromel-aluminum thermocouples inserted into the graphite heater. The behavior of the particles during heating (change in shape, surface structure) was recorded by means of the motion-picture camera RFK-5 with the aid of the MBS-2 microscope. To determine the temperature of a particle, particles (300-500 μm in size) with different melting points were transferred to the graphite plate. The heating of the graphite plate and the motion-picture camera were switched on simultaneously. The moment of fusion of the particle was recorded on the film (in this case the particles assumed the shape close to that of spherical). The melting point of particles was determined using the speed of heating, speed of the film, and the final temperature of the heater.

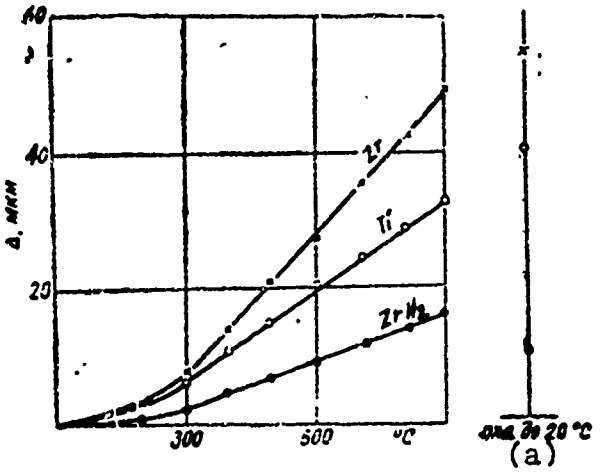
In developing this method (based on several tens of experiments), a graduation graph was plotted and the reliability of temperature determination was verified. The absolute error comprised ±8°.

The experiment was carried out in the following sequence. A small amount of metallic powder of certain fraction was placed on a slide and the size and shape of these particles were estimated by means of the MBS-1 microscope. The particles were measured in two mutually perpendicular directions and the arithmetic mean value was used as the value of the mean diameter. The accuracy in determining the particle size by means of the microscope is ±5 μm.

The particles selected under the microscope (with shape close to that of spherical) were transferred to the center of the graphite heater by means of a special spicule. During the experiment the heating of the graphite plate and the motion-picture camera RFK-5 were activated simultaneously. The particles were heated to 900°. After the experiment the particles, cooled to 20°, were photographed again. In this work we also carried out visual observations (through the microscope) of particle behavior during heating.

The obtained films were processed on a small slide projector DM-2 (total magnification - 290 to 300). The particle size was measured in two mutually perpendicular directions and their average size was determined. The thickness of the oxide film on metal particles was estimated using the difference between the sizes of the oxidized particle and original particle with consideration of thermal expansion. The maximum error in the measurement of thickness of the oxide film was ±1.33 μm.

The figure shows the growth of the oxide film Δ on the zirconium, titanium, and zirconium hydride particles as a function of the heating temperature (Δ - true increase in the diameter of the particle). The behavior of the zirconium and titanium particles is very similar: the interface between the oxide and metal is absent in both of them, i.e., the oxidation can continue even when the particles are coated with a layer of hard oxide. With an increase of temperature from 20 to 200° the increase in the average diameter of a particle is insignificant. Apparently, at these temperatures the dissolution of oxygen can be disregarded [1].



Increase in the oxide film Δ on metal particles as a function of the heating temperature. Particle diameter - 200 μm, heating rate - 30 deg/s. Key: (a) Cooled to 20°C.

The heterogeneous reaction is assumed to occur in the temperature range from 200 to 300° for zirconium and from 300 to 380°

for titanium. (At 200° for zirconium and 300° for titanium the particles change their color and become bluish black, and at 300° for zirconium and 380° for titanium the particles begin to acquire a red color). This process is a slow surface burning. The oxide film formed as a result of reaction covered the remaining part of the metal and prevented the heterogeneous reaction from passing to intensive combustion. With an increase in temperature (from 300° for zirconium and 380° for titanium) to 900° there occurs an intensive rise in thickness of the oxide film on the particles due to the heterogeneous reaction (zirconium 100 μm=Δ=Δ'-δ=35.1 μm, where δ - calculated increase in particles due to thermal expansion, Δ' - mean absolute increase in the particle diameter; 200 μm-Δ= =48.7 μm; 300 μm-Δ=52.4 μm; titanium 100 μm-Δ=33.1 μm; 300 μm-Δ= =36.3 μm.

The heat released during the heterogeneous reaction is expended primarily for heating the entire mass of metal particles in the form of heat conductivity and is partially lost in the surrounding medium. Stresses arise in the oxide film due to an increase in the temperature of the heater (dynamic heating was accomplished in the experiments) and due to the heterogeneous reaction occurring on the surface of metal particles. The stresses increase when the oxygen diffuses inside the particle, as a result, the oxide film cracks and is partially fractured. The nitrogen in the air also facilitates the increase in the breakdown of the oxide film [2, 3]. These occurrences lead to an intensive growth of the oxide film on the zirconium and titanium particles (up to 900°). After cooling the zirconium particles become dull-white, while titanium particles - yellowish-dull in color.

In addition to metals a study was carried out on the preignition processes of zirconium hydride. It is known from the literature data that zirconium hydride is easily ignited [4], however the ignition point of hydride is higher than that of pure zirconium [5].

Under the experimental conditions the behavior of the zirconium hydride particles is similar to that of the zirconium and titanium particles, but with a more complex mechanism; with an increase in temperature from 20 to 200° there is an insignificant increase in the diameter of particles (100 μm-Δ=0.2 μm; 200 μm-Δ= =0.5 μm; 520 μm-Δ=3 μm). In the temperature range from 200 to 300° - start of the heterogeneous reaction. A further heating to 900° leads to an increase in the particle size (100 μm-Δ=7.5 μm; 200 μm-Δ=18.2 μm; 520 μm-Δ=27.5 μm).

Apparently, the oxidation follows the following scheme: dehydrogenation from the particle surface; interaction between the metal and oxygen; interaction between the metal oxide and hydrogen. This oxidation mechanism continues throughout the entire heating process. This also explains the relatively slight increase in the size of zirconium hydride particles. This mechanism is also supported by a decrease in the particle diameter during cooling as a result of a continuing decomposition of the hydride. After cooling the zirconium hydride particles have the color of zirconium oxide.

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